

Electronics of self-assembled nanostructured based on nanocrystallite quantum dots

NSF Functional Nanostructures Grant 9871996

Moungi Bawendi, Klavs Jensen, Ray Ashoori, Paul Laibinis
Massachusetts Institute of Technology

Nanocrystal quantum dots (NCs) of semiconductors (Figure 1) are nanometer size fragments of bulk material. They exhibit optical and electronic properties that are a strong function of their size. The quantum size effect in CdSe quantum dots, for example, is easily observed in their fluorescence as a function of size, shown in Figure 2. NCs are grown as colloids using chemical procedures. Ligands that are bound to their surface give them flexible chemical properties (Fig. 1). The size of NCs, their electronic and optical tunability, and their chemical flexibility make them ideal building blocks for assembling opto-electronic devices at the nanometer scale. NCs also have unique properties that may present powerful opportunities in engineering novel opto-electronic nano-heterostructures. One of these properties is the “blinking” of the fluorescence of individual NCs.

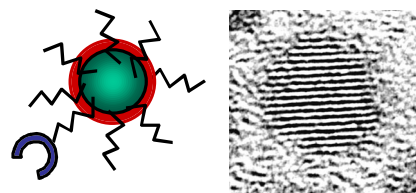


Fig. 1. (left) Cartoon of a NC showing ligands on surface and chemical functional group as a hook. (right) TEM of a single 5 nm NC of CdSe.

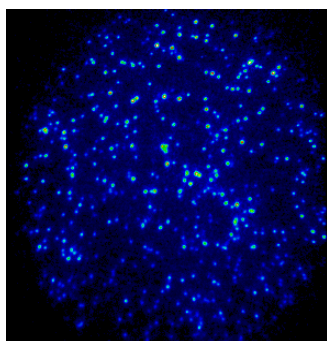


Fig. 3. Single CdSe quantum dots luminescing. The dots are being continuously excited using a laser focused to a 30 micron spot. The image is from a CCD camera and was acquired in 100 ms.

Figure 3 shows an image of individual NCs in a 30 micron spot fluorescing under constant laser illumination. Over time, each of these individual NCs turns on and off in a binary fashion, as shown in Figure 4. This blinking property

was unexpected when it was first observed. It was speculated to be the result of the dots photo-ionizing and charging. Controlling the emission output from one of these individual

nanostructures with the addition or subtraction of a single electron then becomes an attractive proposition in nanoengineering.

The goal of our partnership project is 1) to engineer heterostructures that allow single electrons to be purposely injected into NCs, 2) to explore the fundamental electronic and optical properties of these NC based heterostructures, and 3) demonstrate control over the



Fig. 2. CdSe quantum dots luminescing from blue to red as a function of increasing dot size (1.5- 8nm). (Photograph by Felice Frankel)

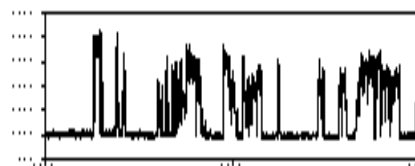


Fig. 4. Time trace over a few minutes of the fluorescence from a single quantum dot.

emission of NCs as a function of charge in these structures. Our strategy has been to first fabricate and study devices based on a few monolayers of NCs placed in a capacitor structure (Figure 5), and then eventually to scale down this device and dilute the NCs so as to probe single NCs as a function of charge. The challenge was to create a capacitor structure that was robust and electrically clean, and where the insulator layer was controlled with nanometer precision with a thickness on the order of 10 to 100 nm. Our approach in this partnership was to create an insulator layer based on the concept of atomic layer deposition (ALD). ALD is a form of CVD where the precursors are cycled in the reaction chamber so as to form a thin film one atomic layer at a time. We chose to develop ALD for ZnS and deposit it as our insulator layer because the processing temperature could be kept low enough (<200°C) to be compatible with NCs. A higher temperature process would have destroyed the NCs. In ALD of ZnS, the Zn and S precursors are introduced in the chamber successively, reacting to form a single atomic monolayer during each cycle. The distinct advantage of this method of depositing thin insulating or semiconducting films is that the films are uniform and atomically smooth over large areas, with a very small pinhole density. These films can be grown with high quality with thicknesses that are as small as 10 nm. We tested deposition of ZnS films directly onto assembled monolayers of NCs and found that the procedure was not deleterious to the NCs. We also tested deposition of monolayers of NCs on top of ALD films of ZnS and found that we could make uniform films of NCs. The capacitor structures were completed by using a transparent ITO electrode on one side and a metal electrode on the other. Cartoons of device structures using ZnS films are shown in Fig. 7.

emission of NCs as a function of charge in these structures. Our strategy has been to first

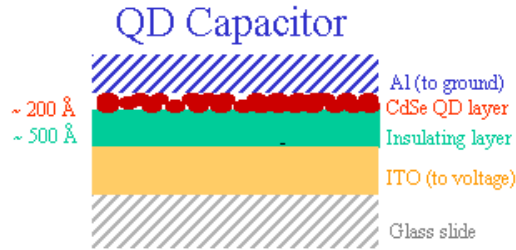


Fig. 5. NC capacitor device structure to controllably charge NCs.

Atomic Layer Deposition: CVD with Sequential Flow of Precursors

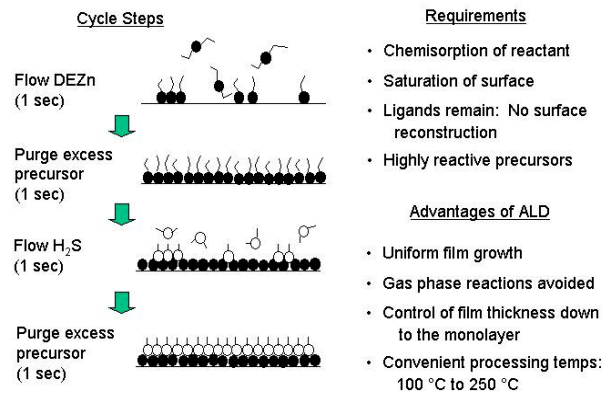


Fig. 6. Description of Atomic Layer Deposition cycles to controllably deposit nanometer thick films of a binary crystalline insulators or semiconductors.

ZnS / NC layer charge injection structures

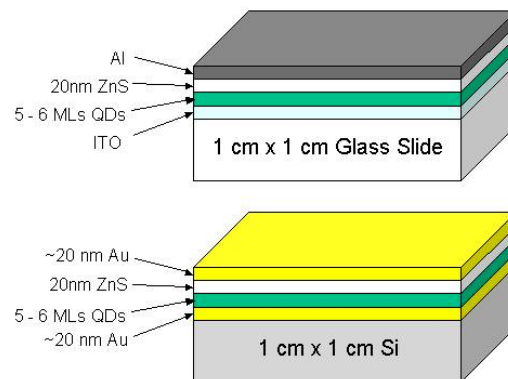


Fig. 7. Cartoon of thin film heterostructures using ZnS as an insulator grown using ALD with the NC layer next to either the ITO or the metal electrode.

The electrical properties of these capacitor structures were tested at room temperature using ultrasensitive capacitance measurements. We found that the capacitance response of the structures was compatible with charge injection into the NC film. As the voltage between the two electrodes is increased and charge is injected into the structure, the capacitance is found to increase, consistent with an increasing charging of the NC layer. Figure 8 shows the frequency dependence of this capacitance as a function of bias voltage. The sharp drop in the capacitance at 10^3 Hz reflects the dynamics of charge injection into the device. At this frequency, the device is no longer responding efficiently to charge injection, at higher frequencies, charge injection becomes difficult. Figure 8 also shows the increase in capacitance with bias voltage, consistent with carrier injection into the film of NCs.

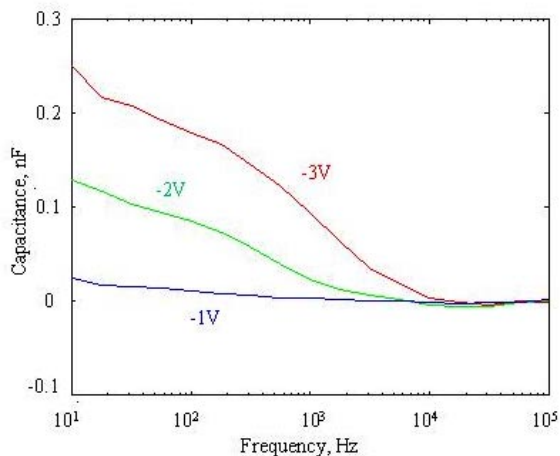


Fig. 8. Capacitance of NC thin film heterostructure as a function of frequency and as a function of bias voltage on the ITO. The increase in capacitance with bias voltage is a signature of carrier injection into the NC film.

The optical response of the device was also tested. Consistent with the hypothesis that a charged nanocrystal is dark, we found that we could reversibly change the emission of the NC layer by charging and discharging it. This result is shown in Fig. 9 as the time trace of the fluorescence intensity as the voltage across the device is applied and then removed. Fluorescence from the NC layer is quenched in Fig. 9 by 70%. The inset shows the fluorescence spectrum of the device with the NC layer charged (quenched) and uncharged. We found that this behavior could be cycled reversibly multiple times.

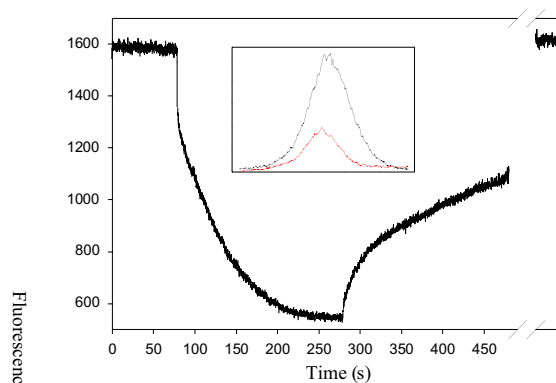


Fig. 9. Fluorescence quenching (70%) as charges are injected in a layer of dots, followed by recovery as voltage is turned off. Inset shows fluorescence spectra of neutral dots (black) and the decreased fluorescence from charged dots (red), demonstrating external control of dot luminescence intensity.

Our experiments demonstrate 1) The development of thin film heterostructures of high electrical quality that incorporate NCs with nanometer accuracy in the vertical direction, 2) the development of high quality nanometer thin insulating and semiconducting films using methodologies that are compatible with the solvent based processing of NCs, 3) the study of the electrical properties of NCs in these thin film geometries, 4) the validation of the hypothesis that charging NCs of CdSe results in a quenching of their emission, and 5) a demonstration of external control of NC luminescence.